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CONCERNING THE PROBLEM OF DISTRIBUTION OF URANYL
NITRATE BETWEEN AQUEOUS SOLUTIONS AND A NUMBER
OF ETHERS AND ESTERS

- USSR -

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CONCERNING THE PROBLEM OF DISTRIBUTION OF URANYL NITRATE
BETWEEN AQUEOUS SOLUTIONS AND A NUMBER
OF ETHERS AND ESTERS

[Following is a translation of an article
by V. M. Vdovenko and Ye. A. Smirnova in
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The extraction method is widely used in chemical analysis, preparatory chemistry and other areas. Nevertheless, literature containing studies of equilibrium distribution from the thermodynamic point of view is relatively scant.

One of the reasons for it is the complexity of distribution processes. In the distribution, uranyl nitrate behaves relatively simply, which enabled Glueckauf, McKay and Mathieson [1] to test distribution data by thermodynamical analysis. They have shown that an uranyl nitrate molecule enters into the organic phase with a certain number of water molecules, and that in the organic phase uranyl nitrate remains mostly not ionized. An equation was reviewed, according to which the distribution of uranyl nitrate between the aqueous and organic phases takes place. Equilibrium constants were determined, as well as the activity coefficient of uranyl nitrate in organic solvents and a series of other quantities, the knowledge of which sheds some light on uranyl nitrate forms in organic solvents.

Glueckauf, McKay and Mathieson developed their thesis in the following way. When uranyl nitrate is distributed equilibrium takes place



where h is the number of water molecules with which each uranyl nitrate molecule goes over into the organic phase. The left part of the equation refers to the organic phase, the right -- to the aqueous.

The equilibrium constant of this reaction can be written as

$$K = \frac{[\text{UO}_2^{2+}][\text{NO}_3^-]^2[\text{H}_2\text{O}]^h}{[\text{UO}_2(\text{NO}_3)_2 \cdot h\text{H}_2\text{O}]}, \quad (2)$$

where brackets indicate the thermodynamic activities.

The product

$$[UO_2^{++}][NO_3]^{-2} = 4 m^3 \gamma^3,$$

where m and γ are the molarity and activity coefficient of uranyl nitrate in aqueous phase.

The activity of hydrated uranyl nitrate in the organic phase can be expressed by Equation

$$[UO_2(NO_3)_2 \cdot nH_2O] = m_u \gamma_u,$$

where m_u and γ_u are the molarity and activity coefficient of uranyl nitrate in the organic phase.

Substituting the expressions obtained into Eq (2) and designating $K_1 = K/4$, we obtain

$$m^3 \gamma^3 a_w^h = K_1 m_u \gamma_u, \quad (3)$$

where a_w is the activity of water. Eq (3) can be written in logarithmic form

$$3 \lg m \gamma a_w^{h/3} = \lg K_1 + \lg m_u \gamma_u \quad (4)$$

or

$$\lg m \gamma a_w^{h/3} = 1/3 \lg K_1 + 1/3 \lg m_u \gamma_u. \quad (5)$$

When $m_u \rightarrow 0$, $\gamma_u \rightarrow 1$ and Eq (5) takes the aspect of

$$\lg m \gamma a_w^{h/3} = 1/3 \lg K_1 + 1/3 \lg m_u \gamma_u \quad (6)$$

Using Equations (4) - (6), Glueckauf, McKay and Mathieson determined quantities K_1 and γ_u for a series of solvents, as based on distribution data.

We investigated uranyl nitrate distribution between water and a series of ethers and esters so as to verify the application of Equations (4) - (6) to the given case and to the determination of quantities K_1 and γ_u . Names, chemical formulas and certain characteristics of ethers and esters discussed are given in Table 1.

All ethers and esters were submitted to prior purification.

Experiments were carried out in the following way. Water solutions of uranyl nitrate in different concentrations was shaken with equal quantities of organic liquids at $t = 25.0 \pm 0.02^\circ$. Equilibrium was usually established after 2-3 hours. The maximum concentration of the equivalent water solution of uranyl nitrate corresponded to a saturated solution at $t = 25^\circ$. For diisopropyl ether, dibutylcarbitol, dimethylphthalate no saturated solutions could be obtained due to the precipitation of uranyl nitrate etherates at high concentrations. After a complete phase separation,

water solution was analyzed for uranyl nitrate content, ether solution -- for uranyl nitrate and water content.

Analyses for uranyl nitrate content were done by ordinary gravimetric method, precipitating ammonium diuranate with subsequent calcination and weighing as U_3O_8 , or by calorimetric method.

Water quantity in the organic phase was determined by Fisher's method as described in Mitcheland Smith's book "Aquametry" [2].

In addition, specific weights of water and ether phases were determined. Graphs for the dependence of $\log m \gamma_u^{h/3}$ on $\log m_u$ were plotted on the base of data obtained (Fig. 1 - 6). Values of γ and a_w were taken from tables for a pure water solution of uranyl nitrate of the same concentration, disregarding the organic solvent dissolved in the water phase of uranyl nitrate, as the solubility of an organic solvent in water is low as a rule, and, therefore, the presence of organic solvent cannot strongly influence quantities γ and a_w . γ and a_w values for different uranyl nitrate concentrations are given below:

Molarity, m	Activity Coefficient γ	Water Activity a_w
0.1	0.573	0.995
0.2	0.543	0.990
0.3	0.540	0.985
0.5	0.564	0.973
0.7	0.616	0.960
1.0	0.721	0.938
1.5	0.959	0.896
2.0	1.288	0.848
2.5	1.67	0.798
3.0	1.12	0.751
3.5	2.47	0.712

Values for h are taken from the precedent work by the authors [3] and are shown in Table 2.

From Figs. 1 - 6, it appears that dependence of $\log m \gamma_u^{h/3}$ on $\log m_u$ is rectilinear (i.e., $\gamma_u = 1$) up to certain $\log m_u$ values.

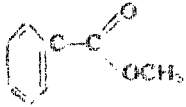
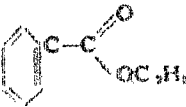
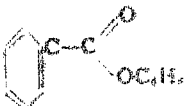
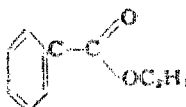
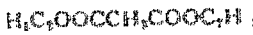
For the majority of organic solvents under consideration, activity coefficient of uranyl nitrate in organic solvent was not equal 1 when $m_u > 0.1$. All straight lines determined have a $1/3$ slope.

Quantities K_1 and γ_u can be determined from the graphs.

Table 1

Organic solvent		Molec. weight	Specific weight (g/cu cm)	Solubility (g per 100 wt parts H ₂ O)	b.p. (°C)	Refraction index	
name	formula					As per Table	Measured
Diethyl ether	<chem>(C2H5)2O</chem>	74.12	0.708 ^{25°}	7.8 ^{20°}	34.6	1.3497	1.3499
Diisopropyl ether	<chem>(C3H7)2O</chem>	102.17	0.722 ^{25°}	0.2	68.5—69.0	1.3678	1.3680
di-n-butyl ether	<chem>(C4H9)2O</chem>	130.22	0.769 ^{20°}	0.05	142.4	1.3992	1.3992
di-isopentyl ether	<chem>(C5H11)2O</chem>	158.28	0.777 ^{20°}	n. p. ^a	173.4	1.7080	1.7079
Chlorex	<chem>(ClCH2CH2)2O</chem>	143.02	1.222 ^{20°}	1.07 ^{20°}	178.5	—	—
Methyl butyrate	<chem>CH3CH2CH2C(=O)OCH3</chem>	102.13	0.898 ^{20°}	1.7	102.3	1.3900	1.3887
Ethyl butyrate	<chem>CH3CH2CH2C(=O)OCH2CH3</chem>	116.16	0.879 ^{20°}	0.68 ^{25°}	120.0	1.3930	1.3935
n-butyl butyrate	<chem>CH3CH2CH2C(=O)OCH2CH2CH2CH3</chem>	144.21	0.872 ^{20°}	n. p.	165.7, P=736 mm	1.4049	1.4055
Isoamyl butyrate	<chem>CH3CH2CH2C(=O)OCH2CH(CH3)CH2CH3</chem>	158.23	0.866 ^{19°}	n. p.	178.6	1.4110	1.4112
Dibutylcarbitol	<chem>C4H9O(CH2)4O(CH2)4OC4H9</chem>	218.33	—	—	254.0	1.4241	1.4241
Ethyl monochloro- acetate	<chem>ClCH2C(=O)OCH2CH3</chem>	122.55	1.159 ^{20°}	n. p.	144.0	1.4216	1.4220
Diethyl succinate	<chem>(CH3CO2C2H5)2</chem>	174.19	1.040 ^{20°}	n. p.	217.0	1.4201	1.4210
Dimethyl phthalate	<chem>C1=CC=C(C(=O)OC)C(=O)OC=C1</chem>	194.18	1.189 ^{25°}	0.43	280.0, P=734 mm	1.5155	1.5155
Diethyl phthalate	<chem>C1=CC=C(C(=O)OCC)C(=O)OCC=C1</chem>	222.23	1.121 ^{25°}	n. p.	298— —299	1.5029	1.5030
n-butyl phthalate	<chem>C1=CC=C(C(=O)OCC)C(=O)OCCCC=C1</chem>	278.34	1.045 ^{21°}	0.04 ^{25°}	346.0	1.4925	1.4930
Ethyl cinnamate	<chem>C1=CC=CC=C1C=CC(=O)OCC</chem>	176.21	1.049 ^{20°}	n. p.	271.0	1.5598	1.5610

Table 1
(continued)

Methyl benzoate		136.14	1.087 ^{25°}	n. p.	198— —199	1.5144	1.5147
Ethyl benzoate		150.17	1.0509 ^{15°}		212.9	1.5054	1.5060
n-butyl benzoate		178.22	1.005 ^{25°}	n. p.	248.5	1.4930	1.4937
Isocamyl benzoate		192.25	0.992 ^{14°}	n. p.	260.0, P=246 mm	1.4940	1.4935
Diethyl malonate		160.17	1.055 ^{20°}	v. t. p.	198.9	1.4162	—

Determination of K_1

In equation (6)

$$\lg m\gamma a_w^{h/3} = 1/3 \lg K_1 + 1/3 \lg m_a$$

when $\lg m_a = 0$

$$\lg m\gamma a_w^{h/3} = 1/3 \lg K_1$$

which permits the determination of quantity K_1 .

Table 2

SOLVENT	$\frac{O}{C}$	h	K_1	V_u (ml/mol)
Diethyl ether	0.25	4.0	2.5	112.0
Diisopropyl ether	0.167	4.0	59.0	111.0
Dibutyl ether	0.125	2.5	421.7	90.5
Diisooamyl ether	0.1	2.2	2900	89.3
β,β' -dichlorodiethyl ether (Chlorex)	0.25	3.8	1738.0	171.4
Dimethyl phthalate	0.4	5.2	15.8	175.0
Diethyl phthalate	0.333	4.2	51.3	164.4
dibutylphthalate	0.25	3.6	331.0	150.0
Methyl benzoate	0.25	4.0	56.9	150.0
Ethyl benzoate	0.222	3.3	105.9	143.6
Butyl benzoate	0.182	2.5	—	137.0
Isoamyl benzoate	0.167	2.5	1318	100.0
Dibutylcarbitol	0.25	4.0	0.76	140.0
Ethyl monochloroacetate	0.5	3.4	257.0	149.1
Ethyl cinnamate	0.182	3.8	64.6	133.33
Diethyl succinate	0.5	5.0	5.6	172.4
Methyl butyrate	0.4	4.0	—	148.0
Ethyl butyrate	0.333	3.5	16.0	143.0
Butyl butyrate	0.25	2.7	—	115.0
Isoamyl butyrate	0.222	2.5	—	128.6
Diethyl malonate	0.57	4.6	8.8	164.0

K_1 values for solvents reviewed are shown in Table 2. Table 2 shows the ratio of oxygen atoms to carbon atoms in each solvent (column 2) the number of water molecules, h , which follow each uranyl nitrate molecule into the organic

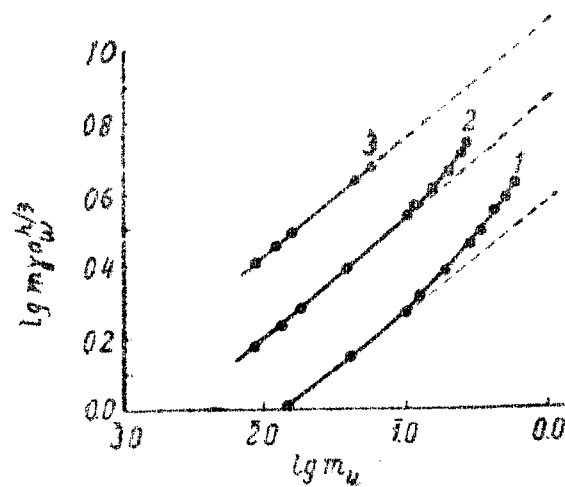


Fig. 1. Dependence of $\log m/a_w^{h/3}$ on $\log m_u$
 1) diisopropyl ether; 2) dibutyl ether; 3)
 chlorex

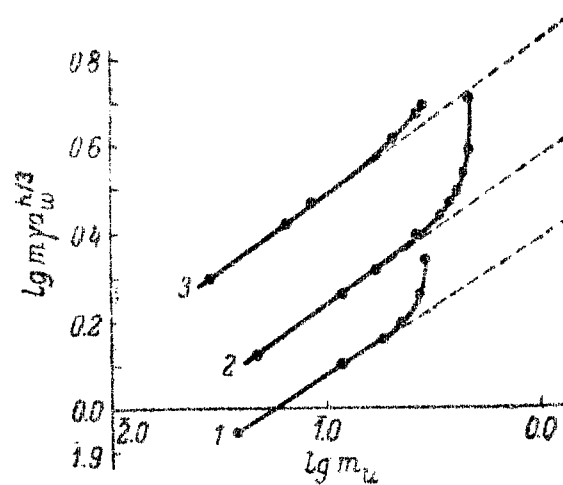


Fig. 2. Dependence of $\log m/a_w^{h/3}$ on $\log m_u$.
 1) dimethylphthalate; 2) diethylphthalate; 3) di-
 butylphthalate.

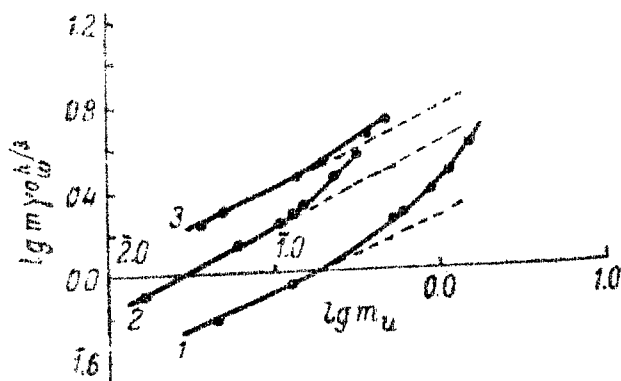


Fig. 3. Dependence of $\lg m/a_w^{h/3}$ on $\lg m_u$.

1) Diethyl succinate; 2) ethyl cinnamate; 3) ethyl monochloroacetate.

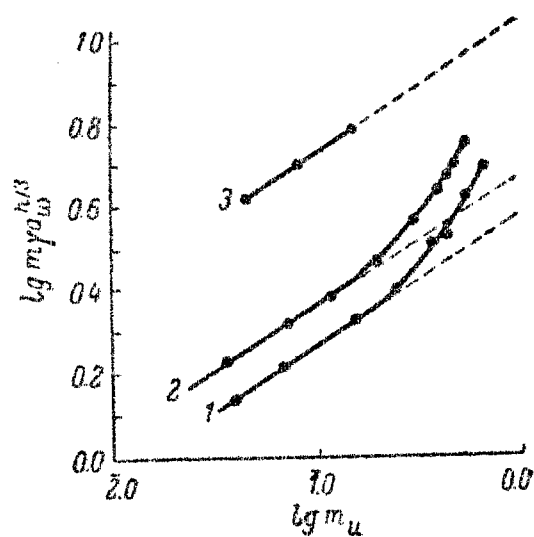


Fig. 4. Dependence of $\lg m/a_w^{h/3}$ on $\lg m_u$.

1) Methyl benzoate; 2) ethyl benzoate; 3) isobutyl benzoate.

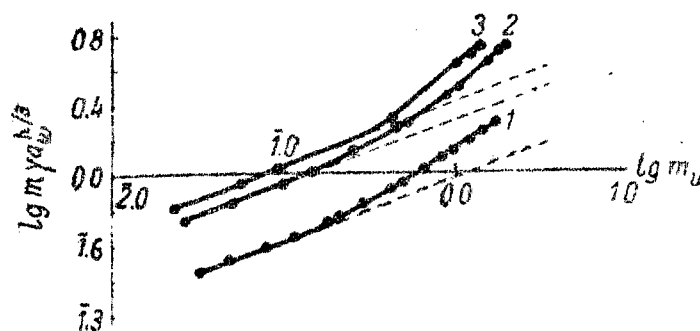


Fig. 5. Dependence of $\log m/a_w^{h/3}$ on $\log m_u$.

1) dibutylcarbitol; 2) diethyl malonate; 3) ethyl butyrate.

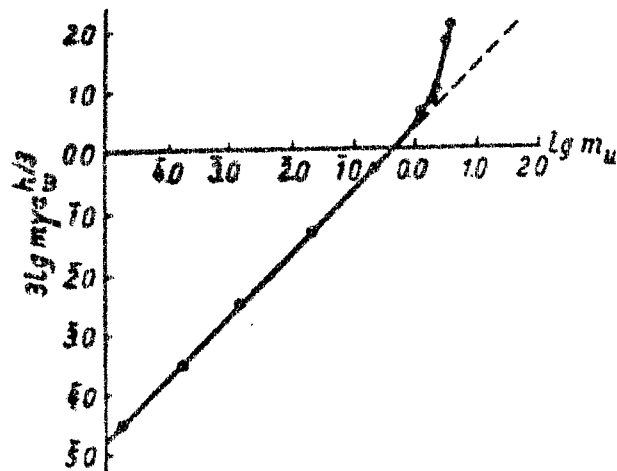


Fig. 6. Dependence of $\log m/a_w^{h/3}$ on $\log m_u$.

1) diethyl ether.

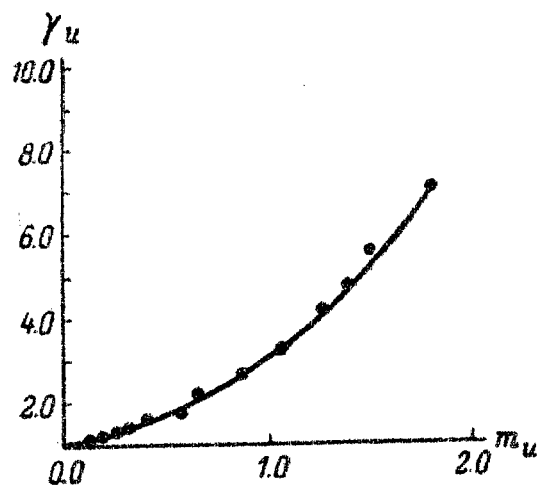


Fig. 7. Dependence of γ_u on m_u for diethyl malonate.

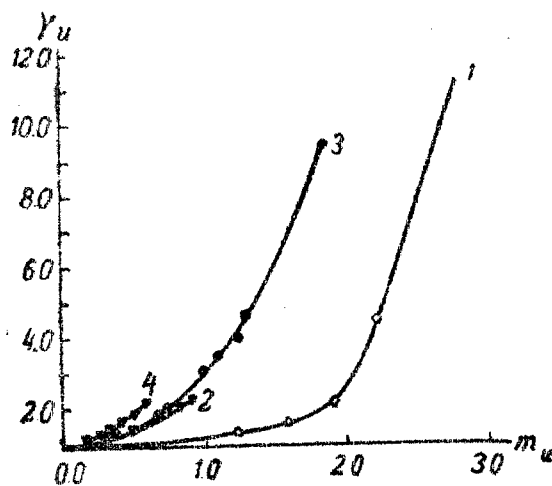


Fig. 8. Dependence of γ_u on m_u .

1) diethyl ether; 2) dibutylcarbitol; 3) diethyl succinate; 4) diisopropyl ether.

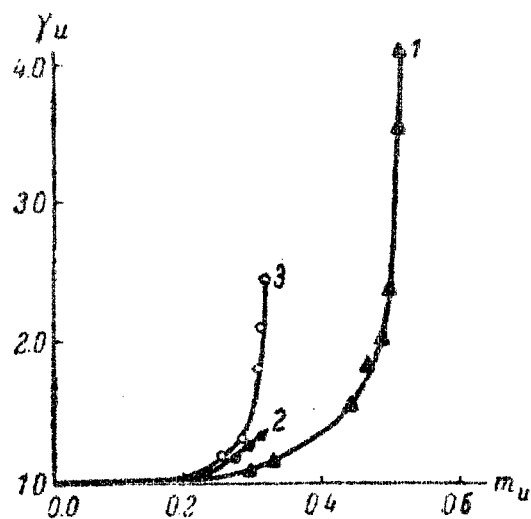


Fig. 9. Dependence of γ_u on m_u .

- 1) dimethyl phthalate; 2) diethyl phthalate;
- 3) dibutyl phthalate.

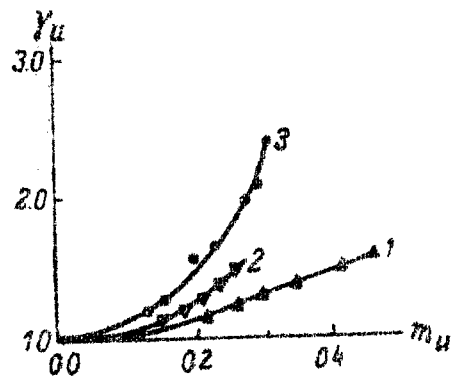


Fig. 10. Dependence of γ_u on m_u .

- 1) ethyl monochloroacetate; 2) dibutyl ether;
- 3) ethyl cinnamate.

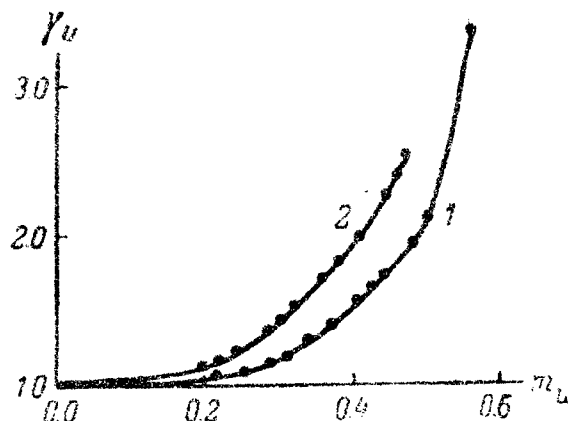


Fig. 11. Dependence of γ_u on m_u .

1) methyl benzoate; 2) ethyl benzoate.

phase (column 3) and the apparent molar volume of hydrated uranyl nitrate in organic solvent V_u (column 5).

As could be expected, one sees from the data of Table 2 that in each of the homological series reviewed quantity K_1 increases when going over from the first members of the series to the higher ones, i.e., extraction capacity decreases. In a series of cases K_1 values strongly differ from each other for solvents having the same ratio of oxygen to carbon atoms (Table 2). This speaks in favor of the influence of groups composing the molecule of the organic solvent and of the electron-donor properties of oxygen atoms.

Extracting capacity of $\beta\beta'$ -dichlorodiethyl ether (chlorex) is 700 times lower than that of diethyl ether.

Such an abrupt drop is apparently caused by the inductive influence of electronegative chlorine atoms in the chlorex molecule on the electron donor properties of the oxygen atom, causing a shift of oxygen electrons toward chlorine electrons.

A negative influence of chlorine atoms on extracting properties is seen in the example of ethyl monochloroacetate.

In addition to the electron-donor properties of solvents, steric-factors play a role in the extraction. Methyl benzoate and dibutyl phthalate having the same electron-donor properties [4] because of equal oxygen: carbon atom ratio, have a different extracting capacity. Maybe a reason for it is a lesser possibility for dibutylphthalate of coordination around uranyl because of greater steric hindrances.

Determination of γ_u

Quantities γ_u can be determined graphically.

As already mentioned before, when uranyl nitrate concentrations in the ether phase exceed 0.1 m_u , experimental curves in Figs. 1 - 6 deviate from rectilinear and γ_u values can be determined according to the deviation from the rectilinear dependence.

To achieve it, $\log m_u$ and $\log m_u \gamma_u$ is determined from the graph, at a fixed $\lg m_w^0 / R$ value, and later -- γ_u quantities for different m_u values.

Data obtained are shown in Figs. 7 - 11. From them it appears that γ_u values increase with the increase of m_u . For a series of solvents $\gamma_u \rightarrow \infty$ at high m_u values.

In conformity with Gibbs - Dygem relation, an increase in γ_u with an increase in uranyl nitrate concentration in the organic phase presumes a decrease in the activity of the solvent, apparently caused by the solvation of the solute by the solvent.

It is characteristic that γ_u does not pass through a minimum. Such a type of dependence is established at present for strong acids and certain salts in nonaqueous solutions, in which acids and salts are practically not dissociated and solvated to a great extent.

Determination of Quantity V_u

(The Apparent Molar Volume of Hydrated Uranyl Nitrate in the Organic Solvent)

Knowing the densities of the organic solvent depending on uranyl nitrate content in it, one can calculate the apparent molar volume of hydrated uranyl nitrate (V_u) in the given organic solvent with the help of the following equation:

$$V_u \cdot m_u = (1000 + 394.1/m_u + m_w \cdot 18.02)/D - (1000 + 18.02 \cdot m_w^0)/D_0 \quad (7)$$

where m_w and m_u are water and uranyl nitrate molarities in the organic solvent, respectively; D -- the density of organic solvent in the presence of uranyl nitrate; m_w^0 -- water solubility in organic solvent; D_0 -- specific weight of organic solvent saturated with water in absence of uranyl nitrate.

For this purpose, a graph is plotted showing the dependence of the first term in the right side of Eq. (7) on m_u , and V_u is determined by the inclination angle of the line. Results so obtained are shown in Table 2. From its data it appears that for the given homological series and going

from a lower member to a higher, quantity V_u decreases.

Comparing V_u quantities for solvents in which uranyl nitrate is approximately equally hydrated, the effect of different molecule packing of organic solvent around uranyl nitrate molecule is noticeable, causing the difference in values of quantity V_u due to a different structure of the organic molecules.

Conclusions

1. It was shown that uranyl nitrate distribution between aqueous solution and a series of ethers and esters is according Eqs (1) - (6).

2. Equilibrium constants of uranyl nitrate between aqueous solution and a series of esters were determined.

3. Activity coefficients and apparent molar volumes of uranyl nitrate in some ethers and esters were determined.

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